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CALORIFIC VALUE OF SOLID FUEL BY THE PARR ADIABATIC BOMB CALORIMETER (1)

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by

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INTRODUCTION

Calorific value is determined in this method by burning a weighed sample in an adiabatic oxygen bomb calorimeter under controlled conditions. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections.

The calorific value is the heat of combustion of a substance. It is usually expressed in British thermal units (BTU) per pound, or in calories per gram.

Gross calorific value is the heat produced by combustion of a unit quantity of solid fuel, at a constant volume, in an oxygen bomb calorimeter under specified conditions such that all water in the products remain in the liquid form.

Net calorific value is a lower value calculated from the gross calorific value. It is equivalent to the heat produced by combustion of a unit quantity of solid fuel at constant atmospheric pressure, under conditions such that all water in the products remain in the form of vapour.

Water equivalent in this method is the calorific value (or sum of heat capacity of water, bucket, bomb and all parts including thermometer, stirrers and bucket supports) required to raise the temperature of the calorimeter one degree celsius.

APPARATUS

The following description may be applied to any calorimeter however the specific readings apply to a PARR #1241 Automatic Adiabatic Calorimeter, #1541 water heater, #1654 Programmer and a #1655 Printer. Specifications may be obtained from the manufacturer.

(1) ASTM Designation: D2015-66 (Reapproved 1972)

METHOD OF DETERMINATION

The balance of a calorimeter is important since the theory of an adiabatic system depends on keeping the temperatures of both jackets identical. To insure that the control is set properly, fill the inner bucket of the calorimeter with water at about 26°C. The apparatus is assembled, turned on, and allowed to equilibrate. When the middle or "orange" light stays on the temperature of both thermometers is noted. Identical readings should be obtained. When the readings are different the balance control knob should be turned either clockwise or counterclockwise to introduce either cold or hot water. Once the proper balance has been achieved the reading on the knob should be recorded and the position locked in. Rechecking this control should be done once a month. When standardizing or determining the water equivalent of the calorimeter a series of ten runs should be completed. For the determinations to be acceptable the standard deviation of the water equivalent values should be no greater than 4 calories per degrees centrigrade. For this purpose no run may be discarded however it may be repeated to achieve the desired standard deviation.

The method of operation while determining water equivalents is the same as the procedure for unknown samples. The standard substance used is S.R.M. Benzoic Acid (6318 calories per gram). The Benzoic Acid pellet should weigh 1.1 grams plus or minus 0.2 grams in order to reproduce a typical temperature rise in the calorimeter.

PROCEDURE

1 - Weigh accurately, to the nearest 0.1 mg, a benzoic acid pellet or fuel sample, into a calorific cruicible.

2 - Into a clean calorimeter bomb place 1.0 ml. of distilled water

3 - Attach a premeasured (10 cm.) calorific fuse wire to the electrodes of the bomb. Leave enough slack to allow this fuse wire to pass through sample.

4 - Assemble bomb

5 - Pressurize the bomb with pure O_2 to 30 atmospheres

6 - Fill bucket with a predetermined weight of water. (The amount of water should be sufficient to entirely submerge the bomb when it is placed in the bucket. The temperature of the water should be close to room temperature. (1-2^{o}C above room temp.)

7 - Place filled bomb in bucket and check for leaks before connecting firing circuit. Position thermometers and stirrers before turning calorimeter on. The calorimeter should run for about 5 minutes until the two thermometers read the same temperature or in this case until the orange light stays on. At this point the programmer button may be pushed. If no programmer is available allow the calorimeter to run another 3 minutes and record the temperature. Push the ignition button and the red light should flash. Leave the calorimeter for another 7 minutes and record the final temperature. However, if a programmer is used the ignition sequence is automatic. The balance control will insure that the temperature of the outer jacket follows that of the inner jacket. After the final temperature is noted remove and disassemble the bomb and check for black unburned particles; if present discard results and repeat. If the run is successful, measure unburned portion of the fuse wire and proceed with calculations.

CALCULATION

Calculations for standardization are somewhat different from those used when calculating the calorific value of an unknown sample, for example:

In standardizing the calorimeter we found that 1.0540 grams of Benzoic Acid produced a temperature rise of 2.869°C. There were 5 units of fuse wire left which we subtracted from the original 23 units to give us a fuse wire correction of 23-5 = 18. We now have the information necessary to calculate the water equivalent according to the formula; $\frac{(Q \times g) + e}{\Delta t} = W$

Where Q = 6318 cal./gram of standard substance (benzoic Acid)
g = 1.0540 g of sample
e = 18 fuse wire correction
Δt = 2.869°C total change in temperature
W = unknown water equivalent

$$\frac{(6318 \times 1.0540)}{2.869} = 2327 \text{ Cal/}^{\circ}\text{C} = W$$

This should be repeated ten times to determine an average water equivalent and the results checked to see if the standard deviation falls within acceptable limits. An example of how the results should be recorded is shown in Table I. Verification of the results are taken from Table II.

TABLE II

Run	Water Sample	Rise in Temperature	Fuse Wire Correction	Water Equivalent
1	0.9882	2.690	23-8=15	2327
2	1.0504	2.862	23-8=15	2324
3	1.1000	2.991	23-9=14	2328
4	1.0008	2.725	23-5=18	2327
5	1.0650	2.903	23-9=14	2323
6	1.0540	2.869	23-5=18	2327
7	1.0222	2.778	23-6=17	2331
8	1.1957	3.258	23-9=14	2323
9	1.0947	2.986	23-8=15	2321
10	1.0168	2.767	23-10=13	2326

TABLE II

Run	Water Equivalent	Absolute Value from Mean	Absolute Value Squared
1	2327	1.3	1.69
2	2324	1.7	2.89
3	2328	2.3	5.29
4	2327	1.3	1.69
5	2323	2.7	7.29
6	2327	1.3	1.69
7	2331	5.3	28.09
8	2323	2.7	7.29
9	2321	4.7	22.09
10	2326	0.3	0.09
TOTAL	23257	23.6	78.10

$$\text{Mean} = \frac{\text{Water Equivalent Total}}{\text{No. of Runs}} = \frac{23257}{10} = 2326$$

$$\text{Standard Deviation} = \sqrt{\frac{\text{Total Absolute Value Squared}}{(\text{No. of Runs} - 1)}}$$

$$= \sqrt{\frac{78.10}{9}} \qquad = \sqrt{8.677}$$

$$= 2.95$$

We now know that the water equivalent determinations are valid and within limits.

To determine the calorific value of an unknown sample, solve for Q in the formula and introduce 2326 for the W value. The formula now reads

$$Q = \frac{(\Delta t \times W) - e}{s}$$

and using the previous example

$$Q = \frac{(2.869 \times 2326) - 18}{1.0540}$$

$$= 6314 \text{ cal/g}$$

GENERAL NOTES

Calorific value determinations must be carried out in duplicate. Duplicate values are acceptable if the difference between the two is less than 0.3 per cent, for example the certified value for standard benzoic acid is 63.8 cal/gm and the determined value found to be 6314 cal/gm. The difference between the certified value and the determined value is:

$$6318 - 6314 = 4 \text{ calories}$$

$$\frac{4}{6318} \times 100 = 0.06\%$$

which is within the accepted tolerance. If the determined duplicates for a coal sample are 7015 and 7040 cal/gm then

$$7040 - 7015 = 25 \text{ calories}$$

$$\frac{25}{7040} \times 100 = 0.3\%$$

In this case the difference is equal to the allowable tolerance and is acceptable. A difference of 30 calories would then be beyond the tolerance and a third determination required.

SULPHUR AND NITROGEN CORRECTIONS

The presence of sulphur and nitrogen in the coal and the nitrogen in the air within the bomb contributes sensible heat in the determination, but would not be available when the coal is burned under atmospheric conditions, and as a result the determined values must be reduced. This correction is normally accomplished by carrying out a tetration to determine the amount of $HaSO_4$ and HNO_3 produced. As a matter of convenience the Analysts Handbook of the National Coal Board 1951 developed a table to simplify these corrections and is reproduced in Table III. The corrections are in calories per gram based on the determined sulphur value and includes the heat contributed by the nitrogen. See example below: (all values are on the as analysed basis)

Sulphur %	1.59	2.68	5.29
Determined cal/gm	6318	7210	7800
Calories contributed S & N from Table III	44	68	127
Corrected cal/gm	6274	7142	7673

CALORIFIC VALUE OF OILS

In the determination of the calorific value of liquid fuels of low volatility the sample weight chosen should be such as to give a temperature rise similar to that of a good coal, a greater sample weight can cause difficulties.

In the determination of the calorific value of liquid fuels of high volatility it is necessary to use gelatine capsules to prevent losses due to evaporation. As the gelatine contributes heat, that due to the gelatine must be taken into consideration. The calorific value of the gelatine must be pre-determined. For example the calorific value of gelatine has been determined as G cal/gm and fits into the following equation:

$$Q = \frac{(W \times \Delta t) - e - (\text{wt of capsule} \times G)}{g}$$

This calorific value must also be corrected for sulphur.

TABLE III

CALORIFIC VALUE OF COAL

CORRECTIONS FOR SULPHUR AND NITROGEN *

Sulphur %	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
0	8	10	12	14	17	19	21	23	26	28
1	31	33	35	37	39	42	44	46	48	51
2	53	55	57	59	62	64	66	68	72	78
3	76	78	80	82	84	87	89	91	93	96
4	98	100	102	104	107	109	111	113	116	118
5	121	123	125	127	129	132	134	136	138	141
6	143	145	147	149	152	154	156	158	161	163
7	166	168	170	172	174	177	179	181	183	186
8	188	190	192	194	197	199	201	203	206	208
9	211	213	215	217	219	222	224	226	228	231
10	233	235	237	239	242	244	246	248	251	253

DIFFERENCE

Sulphur %	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
Cal./g	-	-	-	1	1	1	2	2	2

* Analyst's Handbook: National Coal Board; Hobart House; May 1951